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<b>(54) Title:</b> POLYMER COMPOSITION COMPRISING A MODIFYING AGENT <b>(57) Abstract</b> <p>Novel modifying agents contain a sharply-melting crystalline polymer ingredient, preferably a side chain crystalline (SCC) moiety, and an active chemical ingredient which is physically but not chemically bound to the polymeric ingredient. Such modifying agents, especially when in the form of particles, can be placed in contact with a matrix, will not modify the matrix below the crystalline melting point <math>T_p</math>, but will rapidly modify the matrix above <math>T_p</math>. The active chemical ingredient can react with the matrix, catalyse a reaction of the matrix, or inhibit a reaction of the matrix. Also described are various compositions which comprise (1) a matrix material, e.g. an epoxy resin precursor, (2) a modifying agent containing a sharply melting crystalline polymer ingredient and an active chemical ingredient (which may be physically or chemical bound to the polymeric ingredient), and (3) an additional ingredient which confers desired properties on the mixture or on a product obtained from the mixture.</p>		

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## POLYMER COMPOSITION COMPRISING A MODIFYING AGENT

Our earlier International Application No. PCT/US 96/03023, which had not been published at the priority date of this application, but which was published as  
5 International Publication No. WO 96/27641 on 12 September, 1996, describes

- (A) polymeric modifying agents which comprise (i) a crystalline polymeric moiety which melts over a relatively small temperature range and (ii) an  
10 active chemical moiety which is bonded to the polymeric moiety, preferably through a bond having a strength of at least 10 Kcal/mole;
- (B) compositions comprising (i) a matrix material and (ii) associated therewith, a polymeric modifying agent as defined in (A);
- (C) methods of making chemical compounds in which a composition as  
15 defined in (B), and optionally another material, is subjected to conditions which cause the modifying agent to undergo a physical change which increases the extent to which the matrix material is contacted by the active chemical moiety, and thus causes a chemical reaction of the matrix material; and
- (D) novel products which can be prepared by methods as defined in (C).

20 The polymeric modifying agents (A) are particularly useful for making compositions (B) which are stable for relatively long periods under storage conditions, but which will react rapidly when heated or otherwise treated to increase the contact between the matrix and the modifying agent.

25 In our continuing work in this area of technology, we have made a number of important discoveries, each of which provides a part of the present invention, and which can be combined to provide other important parts of the invention.

30 First Aspect of the Invention

One part of the present invention is our discovery that even when there is no chemical bond between the polymeric and active chemical ingredients of the modifier, and as a result the increase in stability is relatively small, this can be very valuable in  
35 situations in which storage stability is not desired or cannot be achieved in combination with acceptable activity at the reaction temperatures. Under these circumstances it is possible, and may be preferable, to make use of a modifying agent in which the active ingredient is bound to the polymeric ingredient physically but not chemically. Such

modifying agents are referred to herein as "physically bound modifying agents." This may produce a delay (as compared to the active chemical ingredient on its own) which is as short as a few seconds or as long as 12 hours or even more. This delay may result in an increase in one or more of pot-life, cream time (time in hot mold prior to foaming) reaction time, or other reactivity indicator. For example, when highly reactive mixes of polyurethanes or other polymers are being shaped by molding, e.g. by reaction injection molding (RIM), for example when making foamed products, a physically bound modifying agent allows the active chemical ingredients to be released very rapidly, but provides sufficient delay to ensure that curing does not begin before the polymeric mixture is uniformly distributed throughout the mold. Physically bound modifying agents are also useful when a coating is to be cured in place (e.g. with a hot wand) after being applied to a substrate. The invention makes it possible to make up a "day batch" of the coating composition which can be used over a period of several hours. In a physically bound modifying agent, the strength of the association between the ingredients can be influenced by hydrogen bonding and/or physical interaction between the groups on the ingredients, e.g. carboxyl, hydroxyl or other polar groups, or long chain alkyl groups.

Thus, in its first aspect, this invention includes a composition which comprises

- (1) a matrix material; and
- (2) distributed in the matrix material, or adjacent to the matrix material, a modifying agent which
  - (a) comprises
    - (i) a polymeric ingredient which comprises a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P^{0.7}$ , and
    - (ii) an active chemical ingredient which is physically, but not chemically, bound to the polymeric ingredient, and which, when in contact with a matrix material under selected conditions, promotes a chemical reaction of the matrix material, and
  - (b) is in the form of a solid which, when exposed to a change in a variable selected from temperature, concentration of a solvent, electromagnetic radiation, ultrasonic radiation, and pH, undergoes a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which

the matrix material is contacted by the active chemical ingredient, said solid form being selected from

- (i) solid particles which are distributed in the matrix material, and which have one or more of the following characteristics
  - (a) an average particle size of 0.1 to 150 microns,
  - (b) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
  - (c) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer, and
- (ii) a film which is in contact with the matrix material.

The physical association between the polymeric and active chemical ingredients can be of any kind which results (when the selected change in a variable takes place) in the desired increase in the contact between the matrix and the active ingredient. In some embodiments, the ingredients are intimately mixed together. Such mixtures can be prepared, for example by dissolving the ingredients in a solvent and spray drying the resulting solution; or by emulsifying the ingredients in a heated liquid carrier and then cooling the emulsion while shearing. In another embodiment, the active ingredient is surrounded by a coating of the polymeric ingredient. Such compositions can be prepared, for example, by spray drying the active chemical ingredient, suspending the spray-dried powder in a solution of the of the polymeric ingredient, and spray drying the suspension, or in solvent-free systems by forming particles through milling processes.

One of the situations in which it can be useful for at least part of the active ingredient to be present as part of a physically bound modifying agent, i.e. to be physically, but not chemically, bound to the polymeric ingredient, is when the active ingredient is the catalyst for the preparation of a polyurethane, polyurea or polyisocyanurate. Such catalysts include for example compounds containing tin, lead, bismuth or another metal known to catalyze such reactions, e.g. tris(tributyltin) oxide, dibutyltin laurate, tributyl tin acetate, dibutyltin acetoacetate, or tributyl tin methacrylate. In another embodiment, catalysts for use in the curing of unsaturated polyesters (including polyvinyl esters) provide the active chemical ingredient in the modifying agent. Such catalysts include for example compounds containing cobalt, copper, vanadium, manganese, or another transition metal. In these embodiments, the catalyst-containing compound can contain carboxyl, hydroxyl or other polar groups

which can interact with the same or similar groups on the polymer; and a catalyst-containing compound containing long chain alkyl groups can interact with similar groups on an SCC polymer. Thus, by increasing the proportion of units derived from acrylic acid and/or other polar comonomers in an SCC polymer, it is possible to  
5 increase the stability of a modifying agent comprising the SCC polymer and a metal compound containing polar groups. In these embodiments, it is also possible for the modifying agent to contain another active chemical ingredient, which may be another catalytic ingredient or a reactive ingredient. For example, a modifying agent containing a tin compound, e.g. dibutyl tin dilaurate (DBTDL) and a tertiary amine,  
10 e.g. tetraethylene diamine (TEDA), can be prepared for example by mixing the tin and amine compounds with the molten polymer, cooling and forming into particles. Such a modifying agent can also contain a blowing agent, e.g. BL from Air Products. A typical modifying agent would contain 75% SCC polymer, 10% TEDA, 10% DBTDL and 5% BL. The tin compound can be chosen so that it forms a chemical bond with  
15 the polymer, e.g. tributyl tin methacrylate. Alternatively, the amine compound can be chosen so that it forms a chemical bond with the polymer, e.g. dimethylamino ethyl acrylate.

Especially when the matrix material is an epoxy resin precursor and the  
20 modifying agent comprises a polymeric ingredient and an active chemical ingredient which are bound together physically but not chemically, the modifying agent and/or the matrix material preferably comprises enhancing groups, as described below in the fourth aspect of the invention.

#### 25 Second Aspect of the Invention

Another part of the present invention is our discovery that the modifying agents described in the earlier application, and the physical bound modifying agents, can be used successfully with peroxide and azo initiators as the active chemical ingredient.  
30 Thus, in its second aspect, this invention includes a composition which comprises

- (1) a matrix material which will react when exposed to a peroxide or an azo initiator; and
- (2) distributed in the matrix material, a modifying agent which

- (a) comprises

- (i) a polymeric ingredient which comprises a crystalline  
35 polymeric moiety having an onset of melting temperature  $T_0$  and a peak melting temperature  $T_p$  such that  $T_p - T_0$  is less than  $T_p^{0.7}$ , and

- (ii) an active chemical ingredient which contains a peroxy or an azo group, and
- (b) is in the form of solid particles which are dispersed in the matrix material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the peroxide initiator, said solid particles having one or more of the following characteristics
  - (i) an average particle size of 0.1 to 150 microns,
  - (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
  - (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer.

15 Third Aspect of the Invention

Another part of the present invention is our discovery of the valuable results which can be obtained, especially when preparing epoxy resins, through the use of various additives in conjunction with a modifying agent (in which the polymeric  
20 ingredient and the active ingredient can be bound together by a chemical bond only, by a physical bond only, or by both).

Thus, we have discovered that when the active chemical ingredients of the modifying agent promotes a reaction between the matrix material and an added  
25 coreactant, the coreactant preferably has one or more of the following features:

1. It decreases the viscosity of the matrix material.
2. It decreases the latency of the modifying agent.
3. It acts as a coadditive or conditioner, as well as a coreactant.
4. It increases the  $T_g$  of the final product.

30 Preferred coreactants for epoxy resin cures are anhydrides, in particular, methyl tetrahydrophthalic anhydride (MeTHPA). Addition of between about 20% to 50% by weight MeTHPA, preferably between about 25% to 45%, to Epon 828 decreases the viscosity of the epoxy resin by over an order of magnitude from 13,000 cps to 670 cps.  
35 Decreasing the viscosity of the matrix material makes it much easier to add the modifying agent to the matrix material before the mixture becomes too viscous to handle, and makes it possible to increase the proportion of fillers. The anhydride also reduces the latency of the composition, e.g. to 30 days at 25 to 40° C. Such latency

periods are sometimes desired because they indicate that curing will take place rapidly at cure temperatures.

We have also discovered that the addition of low surface energy agents can be useful in improving at least the appearance of polymeric products obtained by reaction of the matrix material. Thus we have found that low surface energy agents prevent the cured resin from exhibiting a rippled surface. It is believed that the rippling occurs because the air-epoxy surface becomes rich in modifying agent and cures fastest, whereas the bulk epoxy phase cures more slowly and shrinks. The low surface energy agents have a lower surface energy than the modifying agent, and are preferentially located at the air-epoxy resin interface. The low surface energy agents thus minimize the accumulation of the modifying agent at the air-epoxy interface and permit a more homogeneous curing process. Preferred low surface energy agents are fluorocarbon surfactants, e.g. Fluorad FC-430 by 3M or Lodyne products from Ciba-Geigy.

15

We have also discovered that the addition of relatively small amounts of certain other coadditives improves at least the appearance of cured epoxy resins without substantially changing the latency characteristics. Preferred coadditives for epoxy resins include alkenyl succinic anhydrides, e.g. nonenyl succinic anhydride available from Humphrey under the tradename K-9 and dodecenyl succinic anhydride. The amount of coadditive is generally 0.5 to 10%, preferably 0.5 to 5%, e.g. 2% to 4%, based on the weight of the epoxy resin. In this weight range the coadditive often improves the uniformity and/or gloss of the cured resin. During incubations of 20 minutes at 177° C, 60 minutes at 120° C, and 120 minutes at 100°C, the cured resin exhibited a minimal amount of chalking when used either as an adhesive or as a coating. The latency of the modifying agent at ambient temperature was not affected. Other preferred coadditives include dodecyl benzene sulphonic acid available under the tradename Nacure 5076, methyl tetra hydro phthalic anhydride, nonyl phenol and pentadec-1-yl phenol. Other additives which we have found useful, especially for improving the surface gloss of highly filled epoxy and epoxy/anhydride systems, include material such as phosphated polyesters (e.g. the material sold by Byk Chemie under the trade name BYK-III) and phosphated and sulfonated titanates such as isopropyl tri(dodecyl) benzene sulfonyl titanate and neopentyl (diallyl) oxy-tri (dioctyl) pyrophosphatotitanate (e.g. the materials sold under the trade names KR95 and Leica 38 by Kenrich Petrochemicals.

35



Generally, the coadditive is added to the matrix material, before or after adding the modifying agent. However, on occasion it may be preferable for some or all of the coadditive to be embedded in the crystalline polymer ingredient, in which case, the coadditive is released therefrom when the modifying agent is heated above  $T_p$ .

5

Thus, the third aspect of the invention includes a composition which comprises

- (1) a matrix material which an epoxy resin precursor; and
  - (2) distributed in the matrix material,
  - (A) a modifying agent which
    - (a) comprises
      - (i) a polymeric ingredient which comprises a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_p$  such that  $T_p - T_O$  is less than  $T_p^{0.7}$ , and
      - (ii) an active chemical ingredient which, when in contact with a matrix material under selected conditions, promotes formation of an epoxy resin from the matrix material, and
    - (b) is in the form of solid particles which are dispersed in the main material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the active chemical ingredient, said solid particles having one or more of the following characteristics
      - (i) an average particle size of 0.1 to 150 microns,
      - (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
      - (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer;
- and a second ingredient, also distributed in the matrix material, which is selected from
- (B1) 20 to 50% by weight, based on the weight of the epoxy resin precursor, of an anhydride;
  - (B2) a surface-active agent having a lower surface energy than the modifying agent; and
  - (B3) 0.5 to 10% by weight, based on the weight of the epoxy resin precursor, of a coadditive which is an alkenyl succinic anhydride;

dodecyl benzene sulphonic acid; methyl tetrahydro phthalic anhydride; nonyl phenol; pentadec-1-yl phenol; a phosphated polyester; a phosphated titanate; or a sulfonated titanate.

5 Fourth Aspect of the Invention

We have also discovered that many of the valuable effects which can be produced by the functional groups of the coadditives, as discussed above and in the earlier application, can also be obtained by attaching such functional groups to the modifying agent or the matrix or both. Such attached groups are referred to herein as  
10 "enhancing" groups. For example, it is possible to make use of (i) a modifying agent which includes, chemically bonded thereto, one or more enhancing groups which are compatible with the matrix or with a product of a chemical reaction of the matrix after the modifying agent has been exposed, and/or (ii) a matrix which includes, chemically  
15 bonded thereto, one or more enhancing groups which are compatible with the crystalline polymer ingredient of the modifying agent.

A particularly valuable use of enhancing groups is to introduce polar groups, particularly carboxyl groups, into the polymeric ingredient of a modifying agent which contains reactive chemical ingredients and which is to be used in making a cured epoxy  
20 resin. We have found that in the absence of such enhancing groups, the cured epoxy resin will not have optimum properties unless the modifying agent is allowed to equilibrate with the matrix before curing takes place. Such equilibration (or "conditioning") may be, for example, for 12-24 hours at 35-40°C. We have found that the need for such conditioning can be reduced or eliminated by introducing carboxyl  
25 groups into the crystalline polymer. In a preferred embodiment, the crystalline polymer contains units derived from maleic anhydride, and the resulting anhydride group is reacted with an amino compound to form an amic acid. The polymer can be for example a copolymer of one or more long chain  $\alpha$ -olefins and maleic anhydride, e.g. Petrolite X8040, or a copolymer of one or more long chain alkyl acrylates, e.g. C22A,  
30 and maleic anhydride. The amino compound may contain the reactive chemical moiety which, when exposed, will take part in the curing of the epoxy matrix, e.g. 1-(2-aminoethyl)-2-methyl imidazole. It is also possible for the residue of the amino compound to be further reacted to provide the active chemical moiety; for example ethanolamine can be reacted with the anhydride group and the resulting amic acid  
35 reacted with 2-ethyl-4-methyl imidazole or 2-methyl imidazole.

Enhancing groups of this type are particularly useful when the modifying agent is physically, but not chemically, bound to the matrix, since conditioning of such modifying agents is apt to cause reaction with the matrix.

5           Thus, a preferred embodiment of the fourth aspect of the invention is a composition which comprises

- (1) a matrix material which is an epoxy resin precursor; and
- (2) distributed in the matrix material, a modifying agent which
  - (a) comprises
    - 10           (i) a polymeric ingredient which comprises
      - (A) a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P$  0.7, and
      - 15           (B) polar groups which reduce the time needed to reach an equilibrium between the matrix material and the modifying agent after they have been mixed, and
    - (ii) an active chemical ingredient which, when in contact
      - 20           with a matrix material under selected conditions, promotes formation of an epoxy resin from the matrix material, and
  - (b) is in the form of solid particles which are dispersed in the matrix material and which, when heated, undergo a physical change
    - 25           which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the active chemical ingredient, said solid particles having one or more of the following characteristics
      - 30           (i) an average particle size of 0.1 to 150 microns,
      - (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
      - (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer;

Another way of overcoming the need to condition the modifying agent in the final mixture is to premix the modifying agent with an epoxy compound which has relatively low viscosity, so that it will accept a high concentration of the modifying agent. The resulting concentrate can readily be dispersed in the final mix. Preferred  
5 low viscosity epoxy compounds are cycloaliphatic epoxy resins, e.g. 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexane-carboxylate, vinyl cyclohexene dioxide, and bis (3,4-epoxy cyclohexyl) adipate, which are available from Union Carbide under the trade names ERL-4221, ERL-4206 and ERL-4299, respectively.

#### 10 Units and Abbreviations

In this specification, parts and percentages are by weight, temperatures are in °C, and  $T_o$ ,  $T_p$  and heat of fusion are determined using a DSC calorimeter (at a rate of temperature change of 10°C/min). The abbreviation CxA is used to denote an n-alkyl  
15 acrylate in which the n-alkyl group contains x carbon atoms, the abbreviation Cx alkyl is used herein to denote an n-alkyl group which contains x carbon atoms, and the abbreviation Cx IEMA is used to denote n-alkyl oxyxycarbonylamidoethyl methacrylates in which the n-alkyl group contains x carbon atoms. Other abbreviations are explained below.

20

#### Matrix Materials

The terms "matrix" and "matrix material" are used in this specification to denote any material or mixture of materials with which the modifying agent is  
25 contacted. The matrix often comprises at least one solid or liquid material which provides a continuous phase in which the modifying agent is distributed. Such a matrix can include, in addition to the modifying agent, one or more other materials which are distributed in the continuous phase of the matrix, for example dissolved or dispersed in the form of particles in the continuous phase. Some such other materials are described  
30 in the sections below entitled Coreactants and Coadditives. Alternatively, for example, the matrix can be in the form of particles, e.g. a fine powder, which is blended with particles of the modifying agent, or in the form of a liquid or gas or solid which is contacted with the modifying agent, for example with one or both surfaces of a film of the modifying agent (the term "film" is used herein to include a layer of the modifying  
35 agent which is supported on a substrate). A matrix in the form of particles may melt at a temperature above or below the melting point of the modifying agent.

The invention is particularly useful for matrix materials which, alone or in combination with other ingredients, are polymerized and/or crosslinked when they are exposed to the active chemical moiety in the modifying agent. These matrix materials include for example cyanoacrylates, epoxy resins, epoxy novolacs, unsaturated poly-  
5 esters, including vinyl esters, and precursors for polyurethanes, polyureas, polyisocyanurates, polycyanurates, polyacrylics and polyphenolics. For further information about matrix materials, reference should be made to International Application No. PCT/US 96/0323.

10 The matrix may be the sole material which takes part in the chemical reaction which is promoted or inhibited by the chemical moiety, or the chemical reaction can involve an additional material, including the coreactants and coadditives discussed below, which is added before or after the modifying agent is treated to change the extent to which the active chemical moiety is exposed to the matrix.

15 Polymeric Ingredients

The polymeric ingredient in the modifying agent can be (or be derived from) a single polymer or from a mixture of polymers, and the polymer can be a homopolymer,  
20 or a copolymer of two or more comonomers, including random copolymers, graft copolymers, block copolymers and thermoplastic elastomers. Preferably at least part of the polymeric moiety is derived from a side chain crystallizable (SCC) polymer, but the invention includes the use of other crystalline polymers having the desired properties.

25 The molecular weight of the polymeric ingredient is an important factor in determining the rate at which the modifying agent diffuses through the matrix. A low molecular weight increases the availability of the reactive ingredient. The number average molecular weight ( $M_n$ ) of the polymeric ingredient is generally 1,000 to  
30 100,000, preferably 1,000 to 50,000. Other factors in determining the rate at which the modifying agent mixes with the matrix is the difference between the solubility parameters of the matrix and the modifying agent, and the crystallinity of the polymeric ingredient (the greater the crystallinity, the lower the rate). Thus an increase in crystallinity generally increases the stability of the composition at temperatures below  
35  $T_p$ , but generally does not change the activity of the modifying agent at temperatures above  $T_p$ . In addition, higher crystallinities often increase the amount of diluents that can be used in the composition. A crystallinity such that the DSC heat of fusion ( $\Delta H$ ) is at least 10 J/g, particularly at least 20 J/g, especially at least 40 J/g, is preferred.

Another factor in determining the rate at which the modifying agent mixes with the matrix above and/or below  $T_p$  is the presence of compatibilizing groups on one or more of the matrix, the modifying agent and coadditives added to enhance the compatibility of ingredients of the composition.

5

It is important that the polymeric ingredient should melt over a relatively small temperature range, so that the extent to which the matrix is contacted by the active chemical ingredient changes sharply when the composition is heated or cooled through the temperature range  $T_0$  to  $T_p$ . The closer  $T_p$  is to room temperature (which for most compositions is the expected or preferred storage temperature), the more rapid the transition should preferably be. Thus  $T_p - T_0$  is preferably less than  $T_p^{0.7}$ , particularly less than  $T_p^{0.6}$ ,  $T_0$  and  $T_p$  being in °C.  $T_p$  can vary widely, e.g. from 10 to 150°C. For compositions which are to be stored at room temperature (typically 20-30°C),  $T_p$  is preferably at least 40°C, particularly at least 45°C, but not more than 100°C, particularly not more than 85°C, so that the modifying agent can be activated by moderate heating above room temperature.  $T_p - T_0$  is preferably less than 10°C, particularly less than 8°C, more particularly less than 6°C, especially less than 4°C.

The SCC polymers which are preferably used as polymeric ingredient in this invention include polymers derived from one or more monomers such as substituted and unsubstituted acrylates, methacrylates, fluoroacrylates, vinyl esters, acrylamides, methacrylamides, maleimides,  $\alpha$ -olefins, p-alkyl styrenes, alkylvinyl ethers, alkylethylene oxides, alkyl phosphazenes and amino acids; polyisocyanates; polyurethanes; polysilanes; polysiloxanes; and polyethers; all of such polymers containing long chain crystallizable groups. Preferred SCC polymers comprise

-Y-

repeating units of the general formula  $\begin{array}{c} | \\ \text{Cy} \end{array}$  where Y is an organic radical forming part of the polymer backbone and Cy comprises a crystallizable moiety. The crystallizable moiety may be connected to the polymer backbone directly or through a divalent organic or inorganic radical, e.g. an ester, carbonyl, amide, hydrocarbon (for example phenylene), amino, or ether link, or through an ionic salt linkage (for example a carboxyalkyl ammonium, sulfonium or phosphonium ion pair). The radical Cy may be aliphatic or aromatic, for example containing alkyl of at least 10 carbons, fluoroalkyl of at least 6 carbons or p-alkyl styrene wherein the alkyl contains 6 to 24 carbons, particularly linear polymethylene moieties containing 12 to 50, especially 14 to 22, carbon atoms, or linear perfluorinated or substantially perfluorinated polymethylene moieties containing 6 to 50 carbon atoms. Polymers containing such side chains can be

prepared by polymerizing one or more corresponding linear aliphatic acrylates or methacrylates, or equivalent monomers such as acrylamides or methacrylamides. The polymers can optionally also contain units derived from one or more other comonomers preferably selected from other alkyl, hydroxyalkyl and alkoxyalkyl acrylates, methacrylates (e.g. glycidal methacrylate), acrylamides and methacrylamides; acrylic and methacrylic acids; acrylamide; methacrylamide; maleic anhydride; and comonomers containing amine groups. Such other co-monomers are generally present in total amount less than 50%, particularly less than 35%, especially less than 25%, e.g. 0 to 15%.

Preferred SCC polymers used in this invention comprise 30 to 100%, preferably 40 to 100%, of units derived from at least one monomer selected from the group consisting of alkyl acrylates, alkyl methacrylates, N-alkyl acrylamides, N-alkyl methacrylamides, alkyl oxazolines, alkyl vinyl ethers, alkyl vinyl esters,  $\alpha$ -olefins, alkyl 1,2-epoxides and alkyl glycidyl ethers in which the alkyl groups are n-alkyl groups containing 12 to 50 carbon atoms, and the corresponding fluoroalkyl monomers in which the thermoalkyl groups are n-fluoroalkyl groups containing 6 to 50 carbon atoms; 0 to 20% of units derived from at least one monomer selected from the group consisting of alkyl acrylates, alkyl methacrylates, N-alkyl acrylamides, alkyl vinyl ethers, and alkyl vinyl esters in which the alkyl groups are n-alkyl groups containing 4 to 12 carbon atoms; and 0 to 15% of units derived from at least one polar monomer selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, vinyl acetate and N vinyl pyrrolidone. Such SCC moieties may also contain units derived from other monomers to change compatibility with the matrix, or to raise the modulus of a reaction product containing the modifying agent; such monomers include styrene, vinyl acetate, monoacrylic functional polystyrene and the like.

For further information about SCC and other polymeric ingredients for use in this invention, reference should be made to International Application No. PCT/US 96/03023.

#### Active Chemical Ingredients and Modifying Agents Containing Them

The selected active chemical ingredient can be a catalytic ingredient (including an initiator), a reactive ingredient, or an inhibiting ingredient. The way in which an ingredient behaves (i.e. as a catalytic, reactive, or inhibiting ingredient) may depend upon the matrix material: for example, an amine group may be catalytic in some

circumstances and reactive in other circumstances. The modifying agent preferably contains at least 1% of the active chemical ingredient. The modifying agent can contain two or more different active chemical ingredients, in which case each can be a catalytic ingredient, or each can be a reactive ingredient, or one or more can be a catalytic ingredient and the other or others a reactive ingredient. The active chemical ingredient can contain, for example, nitrogen, e.g. as a primary, secondary, tertiary or quaternary amine, or as an imidazole or other cyclic structure containing nitrogen; phosphorus, e.g. as a -PR<sub>3</sub> group, where R is an organic radical; oxygen, e.g. as a carboxyl, ester or amide group; a metal or metal-containing group, e.g. a transition metal such as rhodium, cobalt, vanadium or manganese, or a main group metal such as aluminum, bismuth tin, lead, or copper, or a metal alkoxide, for example attached to the polymeric moiety through one or more ligand groups; or a peroxide initiator, e.g. benzoyl peroxide, t-butyl perbenzoate or t-butyl peroctoate.

Chemical ingredients which are particularly useful in this invention include amines (including primary, secondary, tertiary and quaternary amines, and heterocyclic amines such as imidazoles); carboxyl groups; sulfonate groups; phosphines; main group metals, including lead, bismuth and tin; transition metals, including cobalt, copper, manganese, titanium and rhodium, e.g. as [(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> RhCl]<sub>2</sub>, and acetylacetonate esters of transition metals; enzymes; superacids; metal alkoxides; UV-activated moieties, e.g. 4-vinylbenzophenone; Michler's ketone; and acetophenone; and groups which are converted into such groups when the modifying agent is used.

The various parts of this invention can make use of any modifying agent in which an active chemical ingredient is bound (either chemically or physically or both, depending on the part of the invention in question) to a temperature-sensitive polymeric ingredient. The active ingredient can be a catalyst, a reactant or an inhibitor. Reactions which can be catalyzed include polymerizations, e.g. polymerization of one or more olefinically unsaturated monomers (particularly one or more olefins, optionally with one or more substituted olefins), and ring-opening polymerizations, hydrogenations, hydroformylation reactions, enzyme-catalyzed reactions (e.g. in the production of foods, including cheese, and pharmaceuticals, in medical diagnostic procedures, and in the treatment of waste products), oxidations, reductions, etc.

Examples of reactive chemical ingredients, and monomers from which they may be derived, include isocyanato, anhydride, acyl halide, aldehyde, hydroxyl, alkyl or aryl halide, amide, amine, including saturated and unsaturated heterocyclic amine, carboxyl, amine, epoxide, mercaptan, azo and peroxy, and carbamate and urea.



For further information about active chemical ingredients and modifying agents containing them, reference should be made to International Application No. PCT/US 96/03023.

5  
Physical Form of the Modifying Agent

The modifying agent is preferably in the form of solid particles which are uniformly dispersed in the matrix. The matrix may be in the form of a solid or a liquid  
10 which provides a continuous phase including systems which are in the form of particles, with at least some of the particles, viewed individually, comprising a continuous phase of the matrix with particles of the modifying agent dispersed therein. Alternatively the matrix can also be in the form of particles. The smaller the particles, the easier they are to disperse and maintain in a uniformly dispersed state. On the  
15 other hand, the smaller the particles, the lower the ratio of active chemical moieties hidden within the particles to those exposed on the surface of the particles, and the less the potential storage stability of the composition. This ratio decreases as the size of the particles decreases and also is higher for spherical particles than for particles of other shapes. It is, therefore, preferred to use substantially spherical particles having  
20 an average size of 0.1 to 150, more preferably 0.1 to 50, particularly 0.1 to 25, especially 0.1 to 10, microns. Preferably each of the particles is within these ranges. Suitable particles can be produced by known techniques, including spray drying, impact pulverizing, and agitation in a fluid followed by cooling to freeze the particle size.

25  
The modifying agent may also be in the form of a film, which may be self-supporting or a layer on a support.

Relative Amounts of Modifying Agent and Matrix

30  
The relative amounts of modifying agent and matrix may vary widely, depending on the nature and concentration of the active chemical ingredient in the modifying agent, the conditions to which the composition is subjected, and the desired result. Generally the composition contains 0.01 to 50% of the modifying agent. When  
35 the active chemical moiety is a catalytic moiety, the modifying agent preferably contains 1 to 40% thereof, particularly 1 to 10% thereof. When the active chemical moiety is a reactive moiety, preferably the modifying agent contains at least 5%, more

preferably at least 15%, particularly at least 20%, e.g. 15 to 40%, especially 20 to 35%, thereof.

#### Process Characteristics

5

The modifying agent can be contacted with the matrix in any desired way. The resulting composition is then maintained at a temperature below  $T_p$  until the time comes to promote or inhibit the chemical reaction. Heating and cooling are the preferred ways of changing the extent to which the matrix is contacted by the active chemical ingredient. However, other measures can be used in addition to, or instead of, heating or cooling, as described in International Application No. PCT/US 96/03023.

#### Coadditives

15

The compositions used in this invention, which comprise the matrix material and the modifying agent, can contain one or more other ingredients which have a useful effect, and which are referred to herein as coadditives. For example, such an ingredient can (a) help to achieve good distribution of the solid modifying agent in the matrix material and/or reduce the time needed to distribute the solid modifying agent in the matrix; (b) help to stabilize the composition before the treatment which exposes the active chemical ingredient; (c) have a desired effect on the manner or extent to which the active chemical ingredient is exposed by such treatment; (d) have a desired effect on a chemical reaction which takes place after such treatment, e.g. to increase the rate of reaction and/or to lower the temperature at which the reaction takes place; or (e) have a desired effect on the product of such a chemical reaction, e.g. on its stability or its physical characteristics such as strength, toughness, flexibility, color or surface smoothness. A single coadditive can perform two or more of these functions. The total amount of coadditive is preferably 0.05 to 50%, based on the "formula weight". The term "formula weight" is used herein to denote the combined weight of the modifying agent and the matrix, but excluding any non-reactive, e.g. inorganic, fillers.

25

30

For details of such additives, reference should be made to International Application No. PCT/US 96/03023.

35

### EXAMPLES

The invention is illustrated by the following Examples, some of which are comparative examples. Examples 1-20 show the preparation of modifying agents, and  
5 Examples A-F show the use of the modifying agents.

The following abbreviations are used in the description below. C22A is docosanyl acrylate; C18A is octadecyl acrylate; HEA is 2-hydroxyethylacrylate; C1M is methyl methacrylate; MA is maleic anhydride; AA is acrylic acid; DMAEA is N,N-dimethylaminoethyl acrylate; AMZ is 1-(2-aminoethyl)-2-methylimidazole; EMI is 2-ethyl-4-methyl imidazole; 2EZ is 2-ethyl imidazole; AIBN is azo bis (isobutyronitrile); TAP is t-amyl peroxy 2-ethyl hexanoate; BPB is t-butyl peroxybenzoate; C12SH is dodecane thiol; Petrolite is a copolymer of equal parts of maleic anhydride and a mixture of olefins containing an average of 40 carbon atoms, and is available under the  
15 trade name Petrolite 8040;  $M_w$  is weight average molecular weight in Daltons;  $M_n$  is number average molecular weight in Daltons; DGEBA is the diglycidyl ether of Bisphenol A available from Shell under the tradename Epon 828; Kelpoxy G 272-100 is an epoxy resin available from Reichold Chemicals and is a reaction product of an epoxy resin and a mixture of carboxyl-terminated polybutadiene and similar materials sold by B.F. Goodrich under the tradename CTBN; Pluracol is a hydroxy-terminated  
20 polyether available from BASF under the tradename Pluracol P1010; Isonate is 4,4'-methylene bis(phenylisocyanate) available from Dow Chemical under the tradename Isonate 143L; Ancamine 1110 is dimethylamino-methyl phenol available from Air Products Inc.; DBU is diazobicycloundecene from Air Products; D8 is a hydroxy  
25 terminated linear polyester polyol available from Bayer under the tradename Desmophen 800; D1150 is a polyester polyol available from Bayer under the tradename Desmophen 1150; Olin G36-272 is a trifunctional polyol available from Olin Corp.; CB-60N is a polymeric toluene diisocyanate available from Bayer under the tradename Desmodur CB-60N; MRS-4 is a polymeric diphenylmethane diisocyanate  
30 available from Bayer under the tradename Desmodur MRS-4; N-100 is a polymeric hexamethylene diisocyanate available from Bayer under the tradename Desmodur N-100; G-36-232 is a tri-hydroxy functional polyether-polyol available from Olin Chemical Co.; BTBTO is bis(tributyltin) oxide available from Strem Chem Co.; TBT(OAc) is tributyltin acetate available from Strem Chem Co.; DBT(AA) is dibutyltin bis acetoacetate available from Strem Chem Co.; DBTDL is dibutyltin  
35 dilaurate available from Strem Chem Co.; TBTMA is tributyltin methacrylate; Aropol 2036 is a commercially available liquid resin consisting of styrene and an unsaturated polyester polymer which is a mixture of isophthalic acid, a glycol, and maleic acid;

CAT is cobalt (II) acetate tetrahydrate; DICY is dicyandiamide; 2X Viscosity is the time (in days unless otherwise noted) which the composition takes, at the indicated temperature, to double in viscosity. Gel times were measured using a Tecam 3 Gel Timer manufactured by Techne Instruments; a 75 g sample of the material was placed  
5 in a glass jar maintained at the indicated temperature with the plunger of the Gel Timer oscillating in the material. The gel time was the time in minutes taken to "trip" the timer.

#### Example 1

10

C18A (1925 g), C1M (412 g), AA (412 g), C12SH and butyl acetate (3 liters) were mixed. 20% of the mixture was placed in a reaction vessel and heated to 100°C. The remainder of the mixture was added to the reaction vessel over 90 minutes. The temperature was then raised to 110°C and t-amylperoxy benzoate (13.8 g, Esperox  
15 5100 available from Witco) was added, and heating continued for 90 minutes. The resulting polymer (POMA) was dried under reduced pressure and isolated. It had a  $T_O$  of 35°C, a  $T_P$  of 41°C, an  $M_w$  of 85,000 and an  $M_n$  of 15,800.

The POMA and 4,4'-dimethylamino benzophenone (Michler's ketone) were  
20 mixed in a solvent in a ratio corresponding to 1 equivalent of POMA carboxyl group to 0.5 equivalent of the ketone. The solvent was removed under vacuum, and the dried product formed into particles on an air mill, thus providing a modifying agent containing a photoactivatable group.

#### Example 2

25

A physically bound polymeric modifying agent was made as follows. Petrolite (100 g) was heated to 65°C. Ethanolamine (13 g) was then added. After increasing the temperature to 95°C, EMI (28.06 g) was added with stirring.

30

#### Example 3

A copolymer of C22A, AA, and C12SH (96/3/1) having an  $M_w$  of 80,000-100,000 was prepared. A mixture of this copolymer (70 parts) and DBU (30 parts)  
35 was prepared at 80°C, cooled and formed into particles having an average size less than 20 micron.

Example 4

A reaction mixture of C22A (78.6 g), AA (19.6 g), C12SH (1.7 g) in toluene (100 ml) was sparged with nitrogen gas for 20 minutes, followed by addition of AIBN (1 g). The flask was sealed and placed in a thermostatted water bath, with stirring, at 60°C for 20 hours. The reaction mixture was added slowly to 1 liter of acetone with vigorous agitation to precipitate the polymer. The polymer was collected by filtration and washed with acetone. The filtrate was dried in a vacuum oven at 50°C for several hours. Analysis of the C22A/AA/C12SH polymer by gel permeation chromatography (GPC) indicated an  $M_w$  of 23,083 and  $M_w/M_n = 2.38$ .

A physically bound modifying agent was prepared by heating the C22A/AA/C12SH polymer (400 g in 800 ml toluene) and DBTDL (100 g) with stirring until a homogeneous mixture resulted. The mixture was cooled to room temperature, and milled into a fine powder.

Examples 5-14

Examples 5-14 show the preparation of physically bound modifying agents.

The ingredients used in these Examples, and the amounts thereof, are shown in Table 1. In each Example, an SCC polymer of C22A and AA (in the proportions, and having  $T_O$ ,  $T_p$  and  $\Delta H$  values, shown in Table 1) was mixed with the other ingredients shown in Table 1. In Examples 5-9 and 11-14, the resulting solution was heated and spray dried, using a Buchi laboratory spray drier under the conditions shown in Table 2 to yield particles of the size shown in Table 1. In Examples 5-7, the ingredients were simply mixed together before being spray dried. In Example 10, the SCC polymer (8g) and Ancamine (25 g) were mixed at 92°C to form an oil. The oil was emulsified by adding it to stirred water (150 g) which contained 1% polyvinyl alcohol (Mowiol 18-188) and was at 93°C. The mixture was sheared at 2500 rpm for 2 minutes, and then allowed to cool to room temperature while shearing at 1200 rpm. The resulting microcapsules of solidified oil had a particle size of about 30 microns and were collected by filtration. After washing with deionized water, the particles were dried in air for several days; they contained about 55% Ancamine and had a  $T_O$  of 47°C, a  $T_p$  of 50°C and a  $\Delta H$  of 45 J/G. When the product was collected by centrifugation instead of filtration, it contained about 27% Ancamine.

In Example 11, the SCC polymer was melt blended with the DABCO, then dissolved in the chloroform and spray dried. In Example 12, the ingredients were mixed and spray dried at 64°C. In Examples 13 and 14, 2EZ or AMI-2 was dissolved in water and spray dried to yield a fine powder. This fine powder (10 g) was mixed with the SCC polymer (10 g) and heptane (180 ml) at 80°C, and the suspension spray dried to yield a powder in which the particles comprise the 2EZ or AMI-2 surrounded by a coating of the SCC polymer.

TABLE 1

10

Ex. No.	5	6	7	8	9	10	11	12	13	14
C22A	99	95	85	75	95	95	93	99	95	95
AA	1	5	15	25	5	5	7	1	5	5
T <sub>0</sub> (°C)	59	59	60	57	59	59	-	-	59	59
T <sub>p</sub> (°C)	62	63	64	64	62	63	65	-	63	63
ΔH (J/g)	80	74	59	57	80	74	-	-	74	74
SCC	45	45	45	45	30	8	99.4	-	10	10
EMI	15	15	15	15	30	-	-	-	-	-
Chloroform	380	380	380	380	120	-	235	105	-	-
Ancamine	-	-	-	-	-	25	-	-	-	-
DABCO	-	-	-	-	-	-	32	-	-	-
2 EZ	-	-	-	-	-	-	-	12.5	10	-
Heptane	-	-	-	-	-	-	-	-	180	180
AMI2	-	-	-	-	-	-	-	-	-	10
Size (micron)	8	12	9	9	-	30	-	-	-	-

TABLE 2

Example No.	5-8	9	10	12 & 13	14
Feed Pump Setting (ml/min)	3.5	2.3	2.3	2	4
Aspirator Setting (ft <sup>3</sup> /min)	10	7	4	4	11
Nozzle Orifice Size (min)	0.5	0.7	0.7	0.7	0.7
Inlet Temperature (°C)	51	54	41	54	62
Outlet Temperature (°C)	32	41	38	40	52
Atomizing Air (cc/min)	850	720	720	725	800

Examples A to D

In Examples A to D, some of the modifying agents prepared in Examples 1 to 14 were used to prepare crosslinked polymeric resins.

Example A

POMA (20 parts, prepared in Example 1), CIM (50 parts), MA (10 parts), TPGDA (20 parts) were combined at 50°C in the absence of light and then cooled to room temperature. The resin produced (10 parts) was dissolved in toluene (20 ml), coated onto a polyester film at a dry film thickness of 48 microns and subsequently covered with a 38 micron film of polyethylene, to produce a laminatable photoresist which could be activated by heat and light.

Example B

The modifying agents of Examples 6 and 7 were compared with each other and with the unmodified DBU catalyst, in experiments in which they were added to a polyurethane precursor containing D8 (70 parts), Pluracol (30 parts) and MRS4 (38 parts) in an amount equivalent to about 0.3 parts of DBU or 0.3 part DMAEA per 100 parts of polyol. The pot life in minutes at 25°C, measured on 25 ml samples, and the gel time in minutes, measured on 5 g samples on a hot plate, are given in Table 7 below.

TABLE 3

	Ex. 6	Ex. 7	DBU
DMAEA	0.31	--	--
DBU (phr)	--	0.3	0.30
Pot life (mins) 25°C	> 60	30	0.25
Gel time (mins) 80°C	10	2	0

Example C

5

A physically bound modifying agent containing 26% DBTDL was prepared as in Example 3 but replacing the DBU by DBTDL. This modifying agent and DBTDL itself were used with various isocyanate/polyol combinations, in amount such that the mixture contained 0.5 phr of DBTDL versus polyol.

10

The ingredients used and the amounts of the isocyanates and polyols (in parentheses), and the results obtained, are shown in Table 4 below, in which Mod Ag refers to the DBTDL-containing modifying agent.

15

TABLE 4

Ex. No.	Ingredients	Pot Life	Gel Time
C1*	D1150/MRS-4 (100/38)/DBTDL	3:15	1:20
C2	D1150/MRS-4 (100/38)/Mod Ag	4:40	1:40
C3*	D800/MRS-4 (100/67)/DBTDL	3	00:30
C4	D800/MRS-4 (100/67)/Mod Ag	40	00:30
C5*	Pluracol/G36-232/MRS-4 (80/20/29)/ DBTDL	7:45	2:20
C6	Pluracol/G36-232/MRS-4 (80/20/29)/ Mod Ag	14:20	2:20
C7*	D1150/Isonate (100/37)/DBTDL	3:15	1:10
C8	D1150/Isonate (100/37)/Mod Ag	7:15	1:10
C9*	D800/Isonate (100/65)/DBTDL	00:30	00:00
C10	D800/Isonate (100/65)/Mod Ag	5	00:30
C11*	Pluracol/G36-232/Isonate (80/20/28)/ DBTDL	5:30	1:15
C12	Pluracol/G36-232/Isonate (80/20/28)/ Mod Ag	8	1:25
C13*	D800/N-100 (100/99)/DBTDL	8	2
C14	D800/N-100 (100/99)/Mod Ag	>60	1:30



Example D

Various modifying agents identical or similar to the modifying agent of Example 4 (i.e. agents prepared from different monomers and/or monomer ratios and/or different tin chelates) were mixed with a premixed mixture of Pluracol (64 phr), Isonate (20 phr) and G-36-232 (16 phr) to give 0.1 phr of tin. The resulting systems were tested for reactivity at different temperatures by monitoring the gel time. Table 5 below shows the results. Examples D1-D3 serve as controls. Examples D4-D7 use modifying agents with tin covalently bound to the polymeric moiety. Examples D8-D12 use modifying agents in which the tin is physically, but not chemically, bound to the crystalline polymer. Gel times at 20°C are slowest when the tin is covalently bound, but are still substantially slower than the control when the tin is physically bound. Other things being equal, the higher the ratio of AA to tin the longer, the higher the gel time at 20°C and the lower the gel time at 80°C.

TABLE 5

Ex.	Catalyst	AA/T in	% Tin in Catalyst	Gel Time at 20°C	Gel Time at 80°C	Gel Time at 100°C	Gel Time at 120°C
D1	TBT(OAc)	0	34	-	30	6	3
D2	DBTDL	0	19	14	2	<2	<2
D3	DBT(AA)	0	27	-	<2	<2	<1.5
D4	TBT(OAc)/ C22A/AA/C12SH (89/6.7/3.8)	0.43	15	>1400	20	15	15
D5	C22A/TBT MA	0	15	>1400	34	13	7
D6	BTBTO/ C22A/AA/C12SH (89/6.7/3.8)	-	10	>1600	50	20	9
D7	BTBTO/ C22A/HEA/C12SH (76.7/20.8/2.5)	-	6	-	21	9	4
D8	DBT(AA)/ C22A/AA/C12SH (94/1/5)	0.27	5	60	2.25	1.25	1
D9	DBTDL/ C22A/AA/C12SH (86.5/9.6/3.9)	4.13	5	-	>180	>180	>180
D10	DBT(AA)/ C22A/AA/C12SH (86.5/9.6/3.9)	2.58	5	>1400	>120	>120	>120
D11	DBTDL/ C22A/AA/C12SH (93.2/2/3.8)	0.8	4.5	30	15	8	3
D12	DBTDDL/ C22A/AA/C12SH (93.2/2/3.8)	2.1	3.1	55	130	60	60

Example E

A chemically bound modifying agent was made as follows. A solution of C22A (89.4 g), AA (6.7 g) and C12SH (3.8 g) in 100 g of toluene was sparged with nitrogen, and AIBN (0.1 g) was added. The mixture was heated at 60°C for 24 hours, and cooled to about 40°C. 500 ml of methyl alcohol was added with vigorous stirring. The precipitate was collected by filtration, and was dried in a vacuum oven at 50°C to 60°C for 15 hours. Analysis by GPC showed the molecular weight ( $M_w$ ) to be 100,000. A solution of the polymer (175 g) in toluene (350 ml) was warmed to 50°C, and to it was added a solution of 40.7 g (0.163 mole) of cobalt (II) acetate tetrahydrate in 127 ml of warm water. The reaction mixture was heated under reflux for 4 hours to distill the toluene-water azeotrope into a trap, and then heated under reflux 14 hours. The hot reaction mixture was then added slowly to 2 L of acetone with vigorous agitation to precipitate the polymeric product. The precipitate was collected by filtration and dried in a vacuum oven at 60°C overnight. Elemental analysis showed the cobalt level was 5.7 percent. The product was milled to a fine powder having a mean particle size of 4.2 microns.

The modifying agent made in this way was used to cure a mixture of 100 g of Aropol 2036 unsaturated polyester resin and 1.25 g of methylethyl ketone peroxide (MEKP). 0.67 g of the modifying agent and the mixture were vigorously stirred for 5 min by hand to disperse the modifying agent. The gel time of the system at 20°C was 223 min. A control mixture of Aropol 2036 (100 g), MEKP (1.25 g) and 0.6 g of a solution of cobalt naphthenate in mineral spirits (containing 6% elemental cobalt) had a gel time of 16 min.

Other cobalt catalysts and other cobalt catalyst-containing modifying agents were used to cure the same mixture of Aropol 2036 (100 g) and MEKP (1.25 g). All the cured systems reached a modulus of more than  $10^7$  dyn/cm<sup>2</sup> when measured at 30°C and 120°C, and had a  $T_g$  of 120°C-125°C. Details of the catalysts, showing the cobalt content and the molecular weight of the crystalline polymer ingredient, and the results obtained, are shown in Table 6 below. Examples E1-E4 are comparative examples. In the modifying agents in Examples E5 and E6, the cobalt catalyst is physically, but not chemically, bound to the polymeric ingredient. In other Examples, the cobalt catalyst is chemically bound to the polymeric ingredient.

TABLE 6

Example	Catalyst (% elemental cobalt)	g	M <sub>w</sub>	Gel time at 20°C
*E1	-	0	-	8237
*E2	Co(II)naphthenate in mineral spirits (6%)	0.6	-	16
*E3	Co(II) stearate (9.52%)	0.39	-	38
*E4	Co(II) octoate (20.5%)	0.19	-	12
E5	6% Co(II)stearate in C22A/AA/C12SH (93/7/4) (6%)	0.6	-	54
E6	3.5% Co(II) stearate in C22A/AA/C12SH (93/7/4) (3.5%)	1.0	-	255
E7	Co(II)-C22A/AA/C12SH (93/7/4) (4.1%)	0.88	50000	735
E8	Co(II)-C22A/AA/C12SH (93/7/4) (5.4%)	0.67	11185	562
E9	Co(II)-C22A/AA/C12SH (93/7/4) (14%)	0.26	23000	198
E10	Co(II)-C22A/AA/C12SH (80/20/1.5) (5.4%)	0.67	11185	223
E11	Co(II)-C22A/AA/C12SH (82.8/7.2/10) (5.6%)	0.64	3929	120
E12	Co(II)-C22A/AA/C12SH (93/7/4) (5.6%)	0.6	20046	567
E13	Co(II)-C22A/AA/C12SH (72/18/10) (13%)	0.28	3450	1025
E14	Co(II)-C22A/AA/C12SH (72/18/10) (0.5%)	7.2	23000	874
E15	Co(II)-C22A/AA/C12SH (78.8/19.7/1.5) (2%)	1.8	23000	1029
E16	Co(II)-C22A/AA/C12SH (72/8/1.5) (2%)	1.8	19000	3200

Example F

5

The physically bound modifying agents of Examples 5-14, and the active chemical ingredients on their own (for comparative purposes) were mixed with various matrix materials, as set out in Tables 8-10 below, and then tested, with the results shown in Table 11 below. In Tables 8-10, the entry "phr amine" shows the active amine concentration in the mixture.

10

In Examples F1-F4, the modifying agent (1.2 g) and Epon 828 (10 g) were placed in a 20 ml vial and mixed vigorously with a spatula. The samples were tested on a DSC at a heating rate of 10°C/min from 30° to 300°C. In Examples F5-F6, the modifying agent or EMI-24 was hand mixed with the epoxy resin. DSC data were obtained in the same way. Viscosity was measured initially and after 2 days. Lap shear values were obtained by spreading the mixture on 1 x 0.5 inch aluminum coupons with 0.5 inch overlap, heating the sample at 120°C, and measuring the lap shear strength on an Instron Tensile tester with a 1000 lb. load cell at 0.05 inch/min. after the times indicated. The viscosity profiles of the samples over time (rheometer, time sweep, 70°C, 25 rad/sec 20% strain) are shown in Table 7 below.

15

20

TABLE 7

Viscosity after (mins)	0	10	20	30	40	50	55	60	63
Ex F5*	1.5	1.5	3	5	12	51	188	1327	5379
Ex F6	2	3	4	5	9	21	40	102	220

Viscosity after (mins)	66	69	72	75	78
Ex F5*	15930	46160	74940	83080	76660
Ex F6	580	1861	7263	31580	126000

\*Comparative Example

5

In Examples F7-F10, the ingredients were mixed by hand. In Examples F11 and F12, the ingredients were mixed in amounts such that the NCO:OH ratio was 1:1. In Examples F13-F17, the ingredients were mixed by hand, and the results of DSC testing are given in Table 11 as the residual heat of reaction, expressed as a percentage of the initial heat of reaction (which was 300-350 J/g in Examples F13-F15 and 400-600 J/g in Examples F16-F17).

10

TABLE 8

Ex. No	F1	F2	F3	F4	F5*	F6
Mod Agent of Example	Ex. 11	Ex. 12	Ex. 13	Ex. 14	--	Ex 15
EMI 24	--	--	--	--	Yes	--
phr amine	3	3	3	3	5	5
Epon 828	10	10	10	10	85	85
Kelpoxy	--	--	--	--	25	25

15

TABLE 9

Ex. No.	F7*	F8	F9*	F10	F11*	F12
Modify. Agent of Example	-	Ex. 16	--	Ex. 17	--	Ex. 17
Ancamine	Yes	--	--	--	--	--
DABCO 33LV	--	--	Yes	--	Yes	--
phr amine	5	5	5	5	2	2
Epon 828	100	100	100	100	--	--
Olin	--	--	--	--	Yes	Yes
Isonate	--	--	--	--	Yes	Yes

5

TABLE 10

Ex. No	F13*	F14	F15	F16*	F17
Modify. Agent of Example	--	Ex. 18	Ex. 19	--	Ex. 20
2EZ	Yes	--	--	--	--
AMI	--	--	--	Yes	--
phr amine	5	5	5	5	5
Epon 828	10	10	10	10	10

TABLE 11

Example No.	F1	F2	F3	F4	F5*	F6
T <sub>o</sub> (°C)	123	124	128	133	116	112
T <sub>p</sub> (°C)	134	136	139	144	126	128
ΔH <sub>f</sub> (J/g)	244	276	218	222	464	480
Viscosity (poise) 20°C						
initial	--	--	--	--	76	147
after 1 day	--	--	--	--	4132	650
after 8 days	solid	solid	solid	solid	--	--
Lap Shear (psi)						
after 1 hour	--	--	--	--	1960	1870
after 3.5 hours	--	--	--	--	1950	1747

Example No.	F7*	F8	F9*	F10	F11*	F12
T <sub>o</sub> (°C)	105	100	--	--	--	--
T <sub>p</sub> (°C)	122	115	--	--	--	--
ΔH <sub>f</sub> (J/g)	84	91	--	--	--	--
Viscosity (poise)						
initial	x	y	p	q	--	--
after 2 hours	--	--	200p	--	--	--
after 1 day	5 x	y	solid	28 q	--	--
after 2 days	Solid	--	--	--	--	--
after 5 days	--	10 y	--	--	--	--
Gel Time (min)	--	--	--	--	0.1	20

5

Example No.	F13*	F14	F15	F16*	F17
% original enthalpy					
after 1 day	85	92	100	71	87
after 2 days	60	82	89	--	--
after 3 days	--	82	--	46	73
after 4 days	65	--	69	--	--

Example 15

Using the general procedure of Example 1, C18A, C1M, HEA and C12SH  
5 were reacted in a ratio of 70:10:20:1. The dried product (POMHA) had a  $T_p$  of about  
39°C and an  $M_w$  of about 8,700. The POMHA (100 g) was dissolved in  
tetrahydrofuran (500 ml) and cooled to 5°C. Butyl lithium (0.9 equivalents, based on  
hydroxyl groups) is added in drops while maintaining the temperature below 10°C,  
followed by the addition in drops of 4-bromobenzophenone (1.2 equivalents). The  
10 mixture was stirred for 12 hours and filtered. The product (POMBP, a polymer  
containing attached benzophenone) was isolated by precipitation from ethanol and  
dried.

Example 16

15 C22A (1064 g) and C1M (156.4 g) were dissolved in xylene (1530 g). MA  
(570.7 g) was dissolved in xylene (719 g). The C22A/C1M solution was added to the  
MA solution over 1.5 hours at 110°C and concurrently a solution of an initiator (30 g,  
Esperox 5100) in xylene (15 g) was metered in. The temperature was then increased to  
20 130°C. After 2 hours, a further solution of an initiator (15 g, Esperox 5100) in xylene  
(7.5 g) was metered in. After 45 minutes, the temperature was reduced to 25°C.  
AMZ (727 g) was metered in over 1 hours. Xylene (2300 g) was then added, and the  
temperature increased to 130°C. After overnight heating to remove water of  
condensation, the polymeric modifying agent was precipitated with methanol.

Example 17

C22A (77 parts), vinyl imidazole (18 parts) and C12SH (5 parts) were reacted  
in xylene at 125°C in the presence of an initiator (TAP, 1 part). After 2 hours, further  
30 initiator (0.5 part Esperox 5100) was added, and the reaction mixture was maintained  
overnight at 85°C with stirring. At this point, the product could be isolated and  
formed into small particles. Alternatively, it could be mixed with an equal amount of  
epoxycyclohexylmethyl-3,4-epoxy-cyclohexane carboxylate (ERL 4221) in a Cowles  
blender at less than 40°C and then incubated overnight at 40°C to provide a stable  
35 concentrate.

Example 18

A copolymer was prepared by heating C22A (75 g) DMAEA (25 g) and TAP (1%) at 110°C. The copolymer had an  $M_w$  of 15,000-25,000 and a  $T_p$  of 63°C. It was  
5 formed into particles having an average size of 10 microns.

Example 19

To a heated (125°C) vessel was added C22A (924 g), vinylimidazole (VI) (216  
10 g), C12SH (60 g) along with 1% by weight Esperox 570. Over 90 minutes, an  
additional amount of C22A (3700 g), of VI (864 g) and C12SH (240 g) were added  
with 1% Esperox 570. The reaction proceeded for an hour followed by addition of  
0.5% Esperox 5100 and further reaction for two hours. Dodecenyl succinic anhydride  
(4-12% by weight) was added to the hot reaction mixture. Then the reaction product  
15 was cooled, ground, and air milled to particles with a diameter of less than 10 microns.

Example 20

In this example, a solution of the C22A/AA/C12SH polymer prepared in  
20 Example 4 (400 g in 800 ml toluene) was warmed with stirring to dissolve the  
polymer. To the solution was added 324.3 g of BTBTO. The reaction mixture was  
distilled using a Dean-Stark water separator. Water was collected to indicate progress  
of the reaction. When  
10 g of water had been collected, the reaction mixture was added slowly to 3.2 liters of  
25 acetone with agitation to precipitate the polymer. The precipitate was collected by  
filtration, washed with acetone and dried in a vacuum oven at 50°C for several hours.  
The product had a tin content of 13.1%, a  $T_o$  of 37.01°C, a  $T_p$  of 49°C, and a  $\Delta H$  of  
39.6 J/G. It was milled to yield particles with average size of less than 20 microns.



CLAIMS

1. A composition which comprises
- (1) a matrix material; and
- 5 (2) distributed in the matrix material, or adjacent to the matrix material, a modifying agent which
- (a) comprises
- (i) a polymeric ingredient which comprises a crystalline  
10 polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P^{0.7}$ , and
- (ii) an active chemical ingredient which is physically, but not chemically, bound to the polymeric ingredient, and  
15 which, when in contact with a matrix material under selected conditions, promotes a chemical reaction of the matrix material, and
- (b) is in the form of a solid which, when exposed to a change in a variable selected from temperature, concentration of a solvent,  
20 electromagnetic radiation, ultrasonic radiation, and pH, undergoes a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the active chemical ingredient, said solid form being selected from
- (i) solid particles which are distributed in the matrix  
25 material, and which have one or more of the following characteristics
- (a) an average particle size of 0.1 to 150 microns,
- (b) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
- 30 (c) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer, and
- (ii) a film which is in contact with the matrix material.
- 35 2. A composition according to Claim 1 or 2 wherein the modifying agent is in the form of solid particles which are dispersed in a continuous solid or liquid phase of the matrix material.

3. A composition according to Claim 2 wherein
- (a) the matrix material comprises
    - (i) an unsaturated polyester which will undergo a crosslinking reaction when exposed to a metal-containing catalyst, or
    - 5 (ii) chemical compounds which will undergo reaction together when exposed to a metal-containing catalyst to form a polyurethane, polyurea or polyisocyanurate; and
  - (b) the active chemical ingredient is a metal-containing compound which is a catalyst for said reaction of the matrix material.
- 10
4. A composition according to Claim 3 wherein the polymeric ingredient is an SCC polymer, and both the SCC polymer and the metal-containing compound comprise polar groups, and/or both the SCC polymer and the metal-containing compound contain long chain alkyl groups.
- 15
5. A composition according to Claim 1 or 2 wherein the matrix material is an epoxy resin precursor and the polymeric ingredient includes amic acid groups.
- 20
6. A process for making a polyurethane by reacting two or more chemical compounds which comprises
- (A) preparing a composition as claimed in any one of Claims 1 to 4 by a process which comprises mixing the chemical compounds together, at least one of the chemical compounds being the active chemical ingredient in a modifying agent as claimed in Claim 1, and
  - 25 (B) heating the mixture from step (A) to increase the extent to which the matrix material is contacted by the active chemical ingredient.
- 30
7. A process according to Claim 6 wherein a foamed product is made by a reaction injection molding process.
8. A process for making a coated substrate by forming a coating of a heat-curable composition on the substrate, and heating the coating to cure the composition, wherein the heat-curable composition is a composition as claimed in any one of Claims 1 to 5.
- 35
9. A composition which comprises
- (1) a matrix material which will react when exposed to a peroxide or an azo initiator; and
  - (2) distributed in the matrix material, a modifying agent which

- 5
- (a) comprises
- (i) a polymeric ingredient which comprises a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P^{0.7}$ , and
- (ii) an active chemical ingredient which contains a peroxy or an azo group, and
- 10 (b) is in the form of solid particles which are dispersed in the matrix material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the peroxide initiator, said solid particles having one or more of the following characteristics
- 15 (i) an average particle size of 0.1 to 150 microns,
- (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
- (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer.
- 20
10. A composition which comprises
- (1) a matrix material which is an epoxy resin precursor; and
- (2) distributed in the matrix material,
- 25 (A) a modifying agent which
- (a) comprises
- (i) a polymeric ingredient which comprises a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P^{0.7}$ , and
- 30 (ii) an active chemical ingredient which, when in contact with a matrix material under selected conditions, promotes formation of an epoxy resin from the matrix material, and
- 35 (b) is in the form of solid particles which are dispersed in the matrix material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to

which the matrix material is contacted by the active chemical ingredient, said solid particles having one or more of the following characteristics

- (i) an average particle size of 0.1 to 150 microns,
- (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
- (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer;

and

- (B) 20 to 50% by weight, based on the weight of the epoxy resin precursor, of an anhydride.

11. A composition which comprises

- (1) a matrix material which is an epoxy resin precursor; and
- (2) distributed in the matrix material,
  - (A) a modifying agent which
    - (a) comprises
      - (i) a polymeric ingredient which comprises a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P 0.7$ , and
      - (ii) an active chemical ingredient which, when in contact with a matrix material under selected conditions, promotes formation of an epoxy resin from the matrix material, and
    - (b) is in the form of solid particles which are dispersed in the main material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the active chemical ingredient, said solid particles having one or more of the following characteristics
      - (i) an average particle size of 0.1 to 150 microns,
      - (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and

- (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer;

and

- 5 (B) a surface-active agent having a lower surface energy than the modifying agent.

12. A composition according to Claim 11 wherein the surface-active agent is a fluorocarbon surfactant.

10

13. A composition which comprises

- (1) a matrix material which is an epoxy resin precursor; and
- (2) distributed in the matrix material,

- (A) a modifying agent which

15

- (a) comprises

- (i) a polymeric ingredient which comprises a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_P$  such that  $T_P - T_O$  is less than  $T_P$  0.7, and

20

- (ii) an active chemical ingredient which, when in contact with a matrix material under selected conditions, promotes formation of an epoxy resin from the matrix material, and

25

- (b) is in the form of solid particles which are dispersed in the matrix material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the active chemical ingredient, said solid particles having one or more of the following characteristics

30

- (i) an average particle size of 0.1 to 150 microns,
- (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and

35

- (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer;

and

- (B) 0.5 to 10% by weight, based on the weight of the epoxy resin precursor, of a coadditive which is an alkenyl succinic anhydride; dodecyl benzene sulphonic acid; methyl tetrahydro phthalic anhydride; nonyl phenol; or pentadec-1-yl phenol.

5

14. A composition which comprises

- (1) a matrix material which is an epoxy resin precursor; and
- (2) distributed in the matrix material, a modifying agent which
- (a) comprises
- (i) a polymeric ingredient which comprises
- (A) a crystalline polymeric moiety having an onset of melting temperature  $T_O$  and a peak melting temperature  $T_p$  such that  $T_p - T_O$  is less than  $T_p 0.7$ , and
- (B) polar groups which reduce the time needed to reach an equilibrium between the matrix material and the modifying agent after they have been mixed, and
- (ii) an active chemical ingredient which, when in contact with a matrix material under selected conditions, promotes formation of an epoxy resin from the matrix material, and
- (b) is in the form of solid particles which are dispersed in the matrix material and which, when heated, undergo a physical change which causes the modifying agent to lose its physical integrity and increases the extent to which the matrix material is contacted by the active chemical ingredient, said solid particles having one or more of the following characteristics
- (i) an average particle size of 0.1 to 150 microns,
- (ii) a polymeric ingredient having a heat of fusion of at least 20 J/g, and
- (iii) a polymeric ingredient in which the crystalline polymeric moiety is a side chain crystalline polymer;

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15. A method of making a chemical compound which comprises subjecting a composition as claimed in any one of Claims 1 to 5 and 9-14 to the change in the variable which causes the modifying agent to lose its physical integrity.

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/16019

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08L101/00 //(C08L101/00,101:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08L C08G C08K C08J C08F C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LU 57 906 A (L'OREAL) 4 August 1970 see claims 1-12	1
X	DE 16 69 262 A (PLASTIC COATING LTD) 13 May 1971 see page 14, paragraph 3	1
X	WO 94 24219 A (LANDEC CORP) 27 October 1994 see claim 1	1
X,P	WO 96 27641 A (LANDEC CORP) 12 September 1996 see claim 1	1

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PATENT ABSTRACTS OF JAPAN vol. 095, no. 006, 31 July 1995 &amp; JP 07 086465 A (TOSHIBA CORP), 31 March 1995, see abstract</p> <p>-----</p>	1



# INTERNATIONAL SEARCH REPORT

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